# Raman and Infrared spectroscopic characterization of the silicate mineral Lamprophyllite

**Ray L. Frost[a•], Ricardo Scholz[b], Andrés López,[a] Yunfei Xi[a]**

[a] School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

[b] Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG, 35,400-00, Brazil

## ABSTRACT

The mineral lamprophyllite is fundamentally a silicate based upon tetrahedral siloxane units with extensive substitution in the formula. Lamprophyllite is a complex group of sorosilicates with general chemical formula given as $A_2B_4C_2Si_2O_7(X)_4$, where the site A can be occupied by strontium, barium, sodium and potassium; the B site is occupied by sodium, titanium, iron, manganese, magnesium and calcium. The site C is mainly occupied by titanium or ferric iron and X includes the anions fluoride, hydroxyl and oxide. Chemical composition shows a homogeneous phase, composed by Si, Na, Ti, Fe. This complexity of formula is reflected in the complexity of both the Raman and infrared spectra. The Raman spectrum is characterized by intense bands at 918 and 940 $cm^{-1}$. Other intense Raman bands are found at 576, 671 and 707 $cm^{-1}$. These bands are assigned to the stretching and bending modes of the tetrahedral siloxane units.

• Author to whom correspondence should be addressed (r.frost@qut.edu.au)
P +61 7 3138 2407 F: +61 7 3138 1804

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## Introduction

Lamprophyllite is a complex group of sorosilicates with the general chemical formula given as $A_2B_4C_2Si_2O_7(X)_4$, where the site A can be occupied by Sr, Ba, Na and K; B is occupied by Na, Ti, Fe, Mn, Mg and Ca. The site C is mainly occupied by Ti or $Fe^{3+}$ and X includes the anions $F^-$, $OH^-$ and $O^{2-}$. The members of the group are lamprophyllite, barytolamprophyllite, ferroericssonite, lileyite and schüllerite [1]. General chemical formula of lamprophyllite can be written as $(Sr,K,Ba)_2(Na,Ti,Mn^{2+},Fe^{3+})_4Ti_2(Si_2O_7)_2O(O,OH,F)$. The mineral was first described from Kola Peninsula, Russia [2, 3]. The mineral occurs as an accessory mineral in alkaline rocks and was also identified in a number of localities, including Poços de Caldas, Brazil [4], Labrador, Canada [5] and Montana, USA [6].

The crystal structure of lamprophyllite was refined in both monoclinic and orthorhombic symmetry [2, 7], however, only the monoclinic polytype is recognized by the International Mineralogical Association (IMA). The unit cell parameters of lamprophyllite are a = 19.215(5) Å, b = 7.061(2) Å, c = 5.3719(15) Å, β = 96.797(4)° and V = 723.7(4) $Å^3$. The structures of lamprophyllite is based on the *HOH* layer consisting of a central *O* sheet of edge-sharing $Na(1)O_6$, $Na(2)O_6$ and $Ti(2)O_6$ octahedra sandwiched between two heterophyllosilicate *H* sheets. The *H* sheet is built by corner-sharing of Ti(1)O5 square pyramids and $Si_2O_7$ groups and consists of two types of rings of polyhedra: (i) six-membered rings (6*R*) formed by two $Si_2O_7$ groups and two $TiO_5$ square pyramids and (ii) four-membered rings (4*R*) formed by two silicate tetrahedra and two $TiO_5$ square pyramids. The Sr atom is located in the interlayer and is coordinated by six anions from 6*R* of the upper *H* sheet and four anions from 4*R* of the lower *H* sheet.

To the best knowledge of the authors, studies concerning the spectroscopic characterization of the silicate lamprophyllite are rare and is restricted to the database of the University of Arizona, however no interpretation is given. The vibrational spectroscopic characterization of alkaline minerals can be an important tool applied in the study of alkaline pegmatites, due to the complex mineral paragenesis as well as in the mineral exploration.

The objective of this paper is to report the vibrational spectroscopic study of a lamprophyllite mineral and relate the spectra to the molecular chemistry and the crystal chemistry of this complex silicate mineral. We have characterized the mineral lamprophyllite using Raman and infrared spectroscopy, with support of scanning electron microscopy in the mineral characterization.

## Experimental

### *Samples description and preparation*

The lamprophyllite sample studied in this work was obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-139. The sample is from the Rasvumchorr Mt., Khibiny Massif, Russia. . Lamprophyllite sample occurs in association with the silicate minerals cancrisilite - $Na_7(Al_5Si_7O_{24})(CO_3)\cdot H_2O$ and aegirine $NaFe^{3+}Si_2O_6$

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The lamprophyllite sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Scanning electron microscopy (SEM) in the energy dispersive (EDS) mode was applied to support the mineral characterization.

***Scanning electron microscopy (SEM)***

Experiments and analyses involving electron microscopy were performed in the Center of Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil (http://www.microscopia.ufmg.br).

A lamprophyllite fragment up to 2 mm was coated with a 5 nm layer of evaporated Au. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV. A qualitative and semi-quantitative chemical analysis in the EDS mode was performed with a ThermoNORAN spectrometer model Quest and was applied to support the mineral characterization.

**Raman spectroscopy**

Crystals of lamprophyllite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarized light at 633 nm and collected at a nominal resolution of 2 $cm^{-1}$ and a precision of ± 1 $cm^{-1}$ in the range between 100 and 4000 $cm^{-1}$. Repeated acquisitions on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio of the spectra. Spectra were calibrated using the 520.5 $cm^{-1}$ line of a silicon wafer. Previous studies by the authors provide more details of the experimental technique [8-11].

## Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 Fourier transform infrared spectrometer (FTIR) with a smart endurance single bounce diamond attenuated total reflectance (ATR) cell. Spectra over the 4000–525 $cm^{-1}$ range were obtained by the co-addition of 128 scans with a resolution of 4 $cm^{-1}$ and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, Salem, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian-Lorentzian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of $r^2$ greater than 0.995.

## Results and discussion

*Mineralogical and chemical description* The SEM/BSE image of lamprophyllite sample studied in this work is shown in Figure 1. The sample is an anhedral fragment and no zonation or contaminant phases were observed. The mineral was analyzed in the EDS mode and the qualitative chemical composition shows a homogeneous phase, composed by Si, Na, Ti, Fe. Due to the superposition of Kα of Si and Lα of Sr, the characteristic band of Sr is not

show in the EDS spectra. Small amounts of K and Mg are also observed(Figure 2). The presence of P is due to influence of the matrix Fluorine and other anions were not detected.

***Vibrational Spectroscopy***

The Raman spectrum of lamprophyllite in the 100 to 1500 $cm^{-1}$ spectral range is shown in Figure 3a. This figure shows the position and relative intensities of the Raman bands. No intensity was observed over the 1500 to 4000 $cm^{-1}$ spectral range, thus indicating the absence of the water and/or OH units. The Raman spectrum was subdivided into subsections depending upon the type of vibration being studied. The infrared spectrum of lamprophyllite over the 600 to 1800 $cm^{-1}$ spectral range is reported in Figure 3b. This figure displays the position and relative intensity of the infrared bands.

The expansion of the Figure 3a results in the figure given in Figure 4a. This figure shows the Raman spectrum of lamprophyllite over the 750 to 1150 $cm^{-1}$ spectral range. The mineral is fundamentally a silicate $Na_2(Sr,Ba)_2Ti_3(SiO_4)_4(OH,F)_2$. The spectrum is dominated by two intense Raman bands at 918 and 940 $cm^{-1}$. These bands are assigned to the SiO stretching vibrations of the $SiO_4$ units. Dowty showed that the -$SiO_3$ units had a unique band position of 980 $cm^{-1}$ [12] (see Figures 2 and 4 of this reference). Dowty also showed that $Si_2O_5$ units had a Raman peak at around 1100 $cm^{-1}$. There are numerous Raman bands observed at 972, 1001, 1028, 1049, 1072 and 1113 $cm^{-1}$. The Raman bands at 972 and 1072 cm-1 are attributed to the SiO stretching vibration of $Si_2O_5$ units. The complexity of the Raman spectrum is in many ways attributable to the mineral formula. These Raman bands may be assigned to the SiO antisymmetric stretching vibrations of the $SiO_4$ units. The infrared

spectrum of lamprophyllite displays even greater complexity with a wide range of overlapping infrared bands, making the assignment of the infrared bands difficult.

The Raman spectrum of lamprophyllite over the 400 to 750 $cm^{-1}$ spectral range is shown in Figure 5a. This part of the Raman spectrum is domianted by three intense Raman bands at 576, 671 and 707 $cm^{-1}$. The 671 $cm^{-1}$ Raman band is broad and may be resolved into tow components at 671 and 650 $cm^{-1}$. These bands are assigned to the OSiO bending modes of the $SiO_4$ units. Dowty demonstrated the band position of the bending modes for $SiO_3$ units at around 650 $cm^{-1}$. This calculated value is in harmony with the higher wavenumber bands observed at 650 and 671 $cm^{-1}$. The Raman spectrum over the 100 to 400 $cm^{-1}$ spectral range is illustrated in Figure 5b. The two bands at 319 and 349 $cm^{-1}$ are considered to be metal-oxygen (TiO, SrO, BaO) vibrations. The remaining bands at lower wavenumbers are simply described as lattice modes.

**Conclusions**

The mineral lamprophyllite of formula $Na_2(Sr,Ba)_2Ti_3(SiO_4)_4(OH,F)_2$ is fundamentally a silicate based upon $SiO_4$ units with extensive substitution in the formula. Lamprophyllite is a complex group of sorosilicates with general chemical formula given as $A_2B_4C_2Si_2O_7(X)_4$, where the site A can be occupied by Sr, Ba, Na and K; B is occupied by Na, Ti, Fe, Mn, Mg and Ca. The site C is mainly occupied by Ti or $Fe^{3+}$ and X includes the anions $F^-$, $OH^-$ and $O^{2-}$. This complexity of formula is reflected in the complexity of both the Raman and infrared spectra. The Raman spectrum is characterized by intense bands at 918 and 940 $cm^{-1}$. These bands are assigned to the SiO stretching vibrations of the Si2O5 units. Other intense Raman bands are found at 576, 671 and 707 $cm^{-1}$. These bands are assigned to the stretching and bending modes of the $SiO_4$ units.

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**Figure 1 shows a backscattered electron image (BSI) of a lamprophyllite cleavage fragment up to 2.0 mm in length.**

**Figure 2 - EDS spectra of lamprophyllite.**

**Figure 3 (a) Raman spectrum of lamprophyllite over the 100 to 1500 $cm^{-1}$ spectral range (b) Infrared spectrum of lamprophyllite over the 600 to 800 $cm^{-1}$ spectral range**

**Figure 4 (a) Raman spectrum of lamprophyllite over the 750 to 1150 $cm^{-1}$ spectral range (b) Infrared spectrum of lamprophyllite over the 650 to 1150 $cm^{-1}$ spectral range**

**Figure 5 (a) Raman spectrum of lamprophyllite over the 400 to 750 $cm^{-1}$ spectral range (b) Raman spectrum of lamprophyllite over the 100 to 400 $cm^{-1}$ spectral range**